Evaluation of nitrogen effect on ultrasound-assisted oxidative desulfurization process

Matheus A.G. Nunes [a], Paola A. Mello [a], Cezar A. Bizzi [a], Lisarb O. Diehl [a], Elizabeth M. Moreira [b], Wladmir F. Souza [b], Emanuela C. Gaudino [c], Giancarlo Cravotto [c], Erico M.M. Flores [a,*]

[a] *Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil*
[b] *Centro de Pesquisas e Desenvolvimento Leopoldo Américo Miguez de Mello, CENPES/PETROBRAS, 21941-915 Rio de Janeiro, RJ, Brazil*
[c] *Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino, Via P. Giuria 9, 10125 Torino, Italy*

ABSTRACT

A novel procedure based on ultrasound-assisted oxidative desulfurization was applied for diesel oil treatment, which was performed simultaneously to ultrasound-assisted oxidative denitrogenation (UAODN) in order to minimize N interference over S oxidation. The effect of ultrasonic irradiation time, reagent amount and the nature of extraction solvent were evaluated. A petroleum product feedstock containing quinoline was used as a model nitrogen compound and acetic acid and hydrogen peroxide were used as oxidizing agents. Nitrogen removal above 95% was obtained for the model oil after 5 min of ultrasonic irradiation (20 kHz, 750 W, 40%). Additionally, this study showed that quinoline can reduce the oxidative desulfurization efficiency of an oil containing dibenzothiophene. The application of oxidative treatment without ultrasound showed that nitrogen and sulfur removal efficiencies for five diesel oil samples were considerably lower (lower than 22 and 40% for nitrogen and sulfur, respectively). The UAODN procedure was applied for the treatment of a hydrotreated petroleum product feedstock and samples of diesel oil with nitrogen and sulfur content up to 226 and 375 mg kg^{-1}, respectively. Under optimized conditions, nitrogen content below 20 mg kg^{-1} was obtained and the feasibility of ultrasound for simultaneous denitrogenation and desulfurization was demonstrated.

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1. Introduction

The production of diesel oil and other fuels with low levels of polluting compounds is required to meet fuel specifications and thus the removal of some contaminants such as sulfur, nitrogen, oxygen and metals is necessary [1,2]. Hydrodesulfurization (HDS) is currently the industrial refining process used for sulfur removal from petroleum fractions, and it generally occurs simultaneously with hydrodenitrogenation (HDN). In most cases, sulfur and nitrogen compounds are refractory to conventional HDS and HDN processes, and moreover the respective catalysts can be poisoned by nitrogen compounds. In order to overcome these drawbacks, usually the hydrotreatment process has been operated under severe conditions of pressure and temperature (generally from 20 to 100 bar and from 300 to 400 °C, respectively) [2]. Furthermore, pollution caused by NO$_x$ and SO$_x$ emissions has been a critical point to the environment [1,3,4].

Although hydroprocessing has been considered a very important step in petroleum refining industry, it requires expensive processes in cases of deep sulfur and nitrogen removals. In order to satisfy the legislation for commercial fuels, new emerging technologies have been developed and many works on sulfur removal procedures, such as biodesulfurization [5,6], extraction with ionic-liquids [7,8], and oxidative desulfurization (ODS) [9–12] have been reported.

The presence of nitrogen compounds is known to impair desulfurization activity, mainly due to competitive reactions of nitrogen compounds with hydrogen as well as nitrogen adsorption onto catalyst surface [13,14]. The inhibiting effect of nitrogen compounds such as quinoline, indole and carbazole on the hydrodesulfurization process has been observed even at nitrogen concentrations below 15 mg kg^{-1} [15]. Due to this limitation, some non-conventional processes for nitrogen removal have been proposed, resulting in better efficiency. Some of these processes are based on the use of microbiological denitrogenation [16–18], ionic-liquids [19], selective adsorption [20,21] and oxidative denitrogenation (ODN) [22,23].

The oxidative process for desulfurization and denitrogenation is a promising methodology for high efficiency sulfur and nitrogen removal as it can be conducted at relatively low temperature and atmospheric pressure, and does not require hydrogen consumption. In this process, sulfur and nitrogen compounds can be oxidized by some reagents as hydrogen peroxide/formic acid [3], hydrogen peroxide/acetic acid [24] or hydroperoxide/MoO$_3$–Al$_2$O$_3$ [23]. Due to the higher polarity, oxidized sulfur or nitrogen compounds can be removed by a liquid–liquid extraction or adsorption step [22,25–27].

* Corresponding author. Tel.: +55 55 32209445.
   E-mail address: ericommf@gmail.com (E.M.M. Flores).

The use of ultrasound (US) in chemistry can intensify chemical reactions due to several effects, especially those related to cavitation phenomenon [28–30]. Cavitation occurs when mechanical vibrations are generated and transmitted to a liquid medium, producing a series of compression and rarefaction cycles that may exceed the attractive forces of the molecules in the medium, producing cavitation bubbles. In some conditions, the collapse of bubbles in liquids provides a micro-environment with temperature and pressure up to 20,000 K and 1000 atm, respectively [31].

The feasibility of combining oxidizing conditions and US energy for sulfur removal has been proposed in some works [32–36]. However, in a similar way to conventional hydrodesulfurization process, the presence of nitrogen compounds decreases the efficiency of sulfur removal, and most of works do not evaluate the efficiency of ultrasound-assisted ODN, or even the effect of nitrogen in ODS processes.

In the present work, an ultrasound-assisted oxidative denitrogenation (UAODN) procedure using an oxidizing system based on hydrogen peroxide and acetic acid is proposed for the oxidation of nitrogen and its removal from a petroleum product feedstock. The inhibiting effect of quinoline on the oxidative desulfurization of dibenzothiophene was also evaluated. Selected ultrasound-assisted oxidative desulfurization (UAODS) conditions were performed simultaneously to UAODN for the treatment of diesel oils with nitrogen concentration ranging from 86 to 226 mg kg^{-1} and sulfur concentration ranging from 136 to 375 mg kg^{-1}. The effect of S:N molar ratio on UAODS was evaluated from 1:0.1 to 1:2, respectively.

2. Experimental

2.1. Apparatus

Ultrasonic treatment was performed using a 20 kHz and 750 W nominal power ultrasonic processor (Sonics and Materials Inc., Model VC 750, Newtown, USA) with a titanium ultrasonic probe (13 mm diameter, 254 mm long), which was dipped directly into the reaction mixture. Experiments were performed in a 250 mL three-neck conic glass reactor (Sonics and Materials, Inc.) with a glass jacket for temperature control using a circulating water bath (Model MCT 110 Plus, Servylab Ltda., São Leopoldo, Brazil). After US treatment, a glass separator funnel was used for the solvent extraction step. Comparative experiments without US were performed with a high speed mechanical stirrer (Model PT 3100 D, Polytron, Switzerland) using a stainless steel dispersing aggregate (20 mm of diameter) at 2000 rpm.

Analysis of reaction products after quinoline oxidation with acetic acid and H$_2$O$_2$ in toluene was performed using gas chromatography coupled to mass spectrometry (GC–MS, Agilent 6850/5973 Network). Chromatographic and detection conditions are shown in Table 1.

Total nitrogen and sulfur concentration in petroleum product feedstock and diesel oil samples were determined using a total nitrogen and sulfur analyzer with chemiluminescence and fluorescence detectors (direct injection method, Antek Instruments, Model 9000 series nitrogen/sulfur analyzer, Texas, USA), according to ASTM D 4629-96 and D 5453-06 for nitrogen and sulfur determination, respectively [37,38].

A viscometer (Stabinger, Model SVM 3000, Anton Paar GmbH, Graz, Austria) was used for the determination of kinematic viscosity (mm^2 s^{-1}) and density (g cm^{-3}) of samples before and after the treatment according to ASTM D 7042-04 method [39].

2.2. Reagents and materials

In the proposed UAODN procedure, 50% hydrogen peroxide (H$_2$O$_2$, Synth, Diadema, Brazil) and glacial acetic acid (AcOH, C$_2$H$_4$O$_2$, 1.05 kg L^{-1}, Vetec, Rio de Janeiro, Brazil) were used. Quinoline (C$_9$H$_7$N, 98%, Aldrich, St. Louis, USA) was used as a model nitrogen compound for the optimization of process parameters. A synthetic oil solution was then prepared by dissolving quinoline in a hydrotreated petroleum product feedstock, resulting in a solution with total nitrogen concentration of 252 mg kg^{-1}. In order to evaluate the effect of nitrogen content on desulfurization process, dibenzothiophene (DBT, C$_{12}$H$_8$S, ≥98%, Merck, Darmstadt, Germany) was used as model sulfur compound. Quinoline was added to a hydrotreated petroleum product feedstock (similar composition to diesel oil) containing 211 mg kg^{-1} of sulfur (as dibenzothiophene), resulting in S:N molar ratios of 1:0.1, 1:0.3, 1:0.5, 1:1 and 1:2. The properties of the hydrotreated petroleum product feedstock employed in this study are shown in Table 2.

Toluene (C$_7$H$_8$, 0.87 kg L^{-1}), ethanol (EtOH, C$_2$H$_5$OH, 0.79 kg L^{-1}) and methanol (MeOH, CH$_3$OH, 0.79 kg L^{-1}) were purchased from Vetec. Reference solutions for sulfur and nitrogen determination in the oil phase were prepared by dissolving a white mineral oil (AccuStandard, Inc., 5000 mg kg^{-1} sulfur content, New Haven, USA) and pyridine (C$_5$H$_4$N, ≥99.5%, Merck) in toluene. The ultrasonic probe and all the glass materials were cleaned with toluene, ethanol and deionized water.

2.3. Experimental procedures

For the initial experiments, UAODN conditions were similar to those previously optimized for diesel oil desulfurization [40]. In this way, 25 mL of quinoline enriched petroleum product feedstock were heated at 90 °C and sonicated for 9 min running at 40% amplitude with 2.5 mL glacial acetic acid and amounts of 50% H$_2$O$_2$ ranging from 0 to 1.0 mL. After selecting the H$_2$O$_2$ amount, the effect of glacial acetic acid volume (0 to 2.5 mL) was investigated for petroleum feedstock and for diesel oil samples (25 mL). Using the selected reagent amounts, reaction times of 1 to 9 min were investigated and US amplitude of 30 to 70% was evaluated. It is important to point out that all the experiments were carried out at atmospheric pressure (n = 3).

After US treatment, the separation of oil and aqueous phases was spontaneous (less than 1 min), and the oil phase was further extracted by manual shaking using a polar solvent (EtOH, MeOH or H$_2$O) and a glass separator funnel. Nitrogen and sulfur were determined in oil phase after the extraction step in order to evaluate the efficiency of the proposed procedure. Fig. 1 shows the overall procedure and the sequence of optimization performed.

In order to evaluate the quinoline oxidation after UAODN process, 25 mL of quinoline solution in toluene (150 mg kg^{-1} as N), 5 mL of 50%

Table 1
Conditions used in GC–MS for quinoline and oxidative products analysis.

Parameters	Conditions
Injector	
Temperature	250 °C
Carrier gas flow rate (He)	1.2 mL min^{-1}
Injection volume	1 μL
Split/Splitless	20:1
Oven	
Initial temperature	50 °C (3 min)
	80 °C (3 °C min^{-1})
Final temperature	300 °C (10 °C min^{-1}, hold 10 min)
Detector	MS
Temperature	280 °C
Column	HP-5MS (30 m × 0.25 mm × 0.25 μm)

Table 2
Properties of hydrotreated petroleum product feedstock.

Property	Feedstock (oil)	
Hydrogen content (%, w/w)	13.6	
Carbon content (%, w/w)	86.4	
Sulfur (original, mg kg^{-1})	3.6	
Nitrogen (original, mg kg^{-1})	<0.5	
Density 20 °C/4 °C (g cm^{-3})	0.8362	
Distillation temperature (initial b.p., °C)	10% (v/v)	266
	50% (v/v)	328
	90% (v/v)	361